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Title of Invention: Optical disk

Patent Application No.: 63-149845

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### Specifications

1. Title of Invention:

Optical disk

2. Claims:

(1) An optical disk, characterized in that it has a substrate composed of a poly(vinyl cyclohexane) resin with a number average molecular weight greater than 50,000 and a softening point of 150°C or higher.

3. Detailed Explanation of Invention:

#### Field of Use in Industry

This invention concerns an optical disk, in particular, an optical disk which has a substrate formed from a poly(vinyl cyclohexane) resin which has a specific molecular weight and softening point, and which has an excellent heat-processing stability, etc.

### Conventional Technology

Optical recording using lasers has been intensively developed in recent years, since it makes possible high-density information recording, storage, and play-back. An example of this kind of optical recording is the optical disk. In general, optical disks are fundamentally composed of transparent substrates and various kinds of recording media coated on them.

There are many cases in which colorless, transparent synthetic resins are used as the transparent substrates of optical disks; typical examples of these are polycarbonates (abbreviated below as "PCs") and poly(methyl methacrylate) (abbreviated below as "PMMA's"). these resins have excellent colorless transparency and also have their individual intrinsic excellent properties, but they do not have all of the essential properties required for optical materials, especially optical disk substrates, and therefore have problems which require solution. For example, PCs have the problem of birefringence, caused by their aromatic rings, and they also have the problem of water absorbability or permeability. PMMA's, on the other hand, have been found to have various problems, such as their heat resistance, water absorbability, and toughness.

Thus, these resins have been used, despite their own intrinsic problems, but in reality, new problems, which are described below, arise in relationship to the recording media coated on the transparent substrates made with these resins.

On the other hand, with respect to recording media, developments in many directions have been performed related to the applications of the optical disks. For example, among recording and play-back media, referred to as the "write-once" type, there is the type in which holes are made, and among recording/play-back/erase/re-recording media, referred to as the "erasable" type, there is the phase transfer type, which uses the crystal transfer phenomenon, the optomagnetic type, which uses the optomagnetic effect, etc. These recording media materials consist primarily of tellurium and its oxides, synthetic compounds, etc. in the case of the write-once type, and amorphous alloy compounds, etc., of rare earth and transition metals, such as GdFe, TbFe, GdFeCo, and TbFeCo, as well as inorganic materials in the case of the erasable type. In general, they are formed by forming films on the transparent substrates by dry methods, such as sputtering in high vacuums.

The moisture absorbability and water permeability of PC and PMMA cause problems of warping due to expansion of the substrate itself when it absorbs moisture; on the other hand, however, by allowing moisture to permeate through the substance, decomposition of the recording medium is caused, and this results in a shortening of the life of the optical disk substrate.

Moreover, the heat resistance of the substrate resin causes the following problems. In optical disks, especially those of the write-once and erasable types, the temperature of the optical disk reaches 200°C or higher during writing and erasing. Therefore, even if this heat does not directly fall on the disk substrate, it can be predicted that the substrate will become rather hot during writing and erasing, and resins with low heat resistances can give problems, such as deformation of the substrate or deformation of grooves.

On the other hand, in the process of manufacturing optical disks, heat treatment processes are frequently included in order to prevent the substrates or recording media from changing over time, but in order to improve productivity, it is desirable to shorten the processing time by performing the treatment at as high a temperature as possible. From this point of view, if the heat resistance of the resin is low, a high treatment temperature cannot be employed, and the productivity cannot be increased.

Therefore, PMMA, which has a low heat resistance is completely inadequate for withstanding the high temperatures of the optical disk production process or the conditions under which optical disks are used, and PC, with a higher heat resistance, has been primarily investigated up to now as a transparent substrate material. However, even PC has been evaluated as not necessarily having sufficient heat resistance, and the appearance of resin materials with higher heat resistances is desired.

As a way of compensating for the drawbacks in conventional resins, such as PC and PMMA, the method of using poly(vinyl cyclohexane) resins as optical disk substrates has been proposed in Japan Public Patent Disclosure Bulletin No. 63-43910 and Japan Patent Application No. 62-157324.

### Problems Which This Invention Seeks to Solve

However, even when poly(vinyl cyclohexane) resins are used, one cannot necessarily obtain optical disk substrates with high performances, and satisfactory results with respect to heat resistance, etc., have not yet been obtained.

The inventors performed careful investigations into the problems of manufacturing optical disks using poly(vinyl cyclohexane) resins, which were proposed in the aforementioned patent applications, as the substrate materials, and obtained the following findings.

Poly(vinyl cyclohexane) resins are ordinarily obtained by the hydrogenation of the aromatic ring of a vinyl aromatic polymer; in general, they are known as brittle polymers, like polystyrene.

In optical disks of the write-once and erasable types, as mentioned above, a considerable thermal history is received in the conditions of use and production process, so that a high heat resistance is required for the resin substrate. Moreover, a degree of toughness is required which is at least sufficient so that the disk substrate resin material is not damaged during the mold release time during the injection molding.

From this point of view, the inventors investigated the manufacturing of optical disk substrates by using poly(vinyl cyclohexane) resins which were mentioned in the aforementioned previous applications. As a result, they found that the aforementioned required properties were insufficient in the polymers disclosed in these applications. That is, in the case of polymers with high ring hydrogenation rates and high heat resistances, the molecular weights are low and damage is produced during the injection molding. Therefore, satisfactory disk substrates were not obtained. On the other hand, with polymers with little reduction in molecular weight, the ring hydrogenation rates were low, and their heat resistances were insufficient.

This invention has the purpose of solving the aforementioned problems with the conventional technology by providing optical disks with substrates made from poly(vinyl cyclohexane) resins with excellent heat resistances and good moldabilities.

### Means for Solving These Problems and Operation of Invention

The optical disk of this invention is characterized in that it has a substrate composed of a poly(vinyl cyclohexane) resin with a number average molecular weight greater than 50,000 and a softening point of 150°C or higher.

That is, the inventors discovered, as a result of careful investigations into improving the heat resistances and moldabilities of the aforementioned poly(vinyl cyclohexane) resins, that optical disks could be obtained, with high productivity, which could be used effectively even under severe heat conditions, such as those of the write-once and erasable types, by using poly(vinyl cyclohexane) resins with specific molecular weights and softening points.

If the number average molecular weight of the poly(vinyl cyclohexane) resin used in this invention is 50,000 or less, the toughness of the resin will be poor, and if the softening point is lower than 150°C, the substrate will be warped or the grooves will be deformed by the heat of the writing and erasing in the case of write-once, erasable, etc., optical disks. Moreover, the heat processing temperature during the process of manufacturing the optical disks must be lowered, and the productivity will be reduced, especially in comparison with PC, which was investigated formerly.

This invention will be explained in detail below.

The poly(vinyl cyclohexane) resin used in this invention is obtained preferably by ring-hydrogenating a styrene polymer.

As the styrene polymer raw material, one can use vinyl aromatic hydrocarbon polymers or vinyl aromatic hydrocarbon block copolymers. Examples of the latter vinyl aromatic hydrocarbon block copolymers are ones composed of a vinyl aromatic hydrogen polymer segment (abbreviated below as the "A segment") and at least 1 conjugate diene polymer segment (abbreviated below as the "B segment").

Examples of the vinyl aromatic hydrocarbon polymer used as the monomer are styrene, p-methylstyrene,  $\alpha$ -methylstyrene, etc. An especially typical example is styrene.

Homopolymers composed of 1 of these vinyl aromatic hydrocarbons or copolymers of 2 or more of them can be used as the vinyl aromatic hydrocarbon polymer. In cases in which

especially good adhesiveness, etc., is required, it is desirable to use a copolymer obtained by copolymerizing the aforementioned vinyl aromatic hydrocarbon with an unsaturated monomer which is copolymerizable with it and has a polar group, in a range such that the properties of the vinyl aromatic hydrocarbon polymer are not lost.

Next, as the A segment in the vinyl aromatic hydrocarbon block copolymer, one can use the same vinyl aromatic hydrocarbon polymers as those mentioned above. Moreover, as the conjugate dienes of the B segment in the vinyl aromatic hydrocarbon block copolymer, one can use 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene, etc. In particular, 1,3-butadiene and isoprene are generally used. The block copolymer obtained from the A segment and the B segment can be obtained easily by the publicly known method called "living anion polymerization"; for example, one can polymerize in hydrocarbon solvents such as hexane, heptane, etc., with organic lithium compounds used as initiators. Furthermore, the content of the A segment of such block copolymers should be 80 wt % or more, preferably 90 wt % or more, and especially preferably 93 wt % or more. If the content of the A segment is less than 80 wt %, the heat resistance of the resin obtained after the hydrogenation is reduced, and it will be unsatisfactory as an optical disk substrate.

In this invention, the molecular weight of raw material styrene polymer should be a number average molecular weight of 80,000 or more. If the molecular weight of the styrene polymer is too low, the heat resistance and toughness of the resin obtained after the hydrogenation will be reduced. The reduction in toughness accompanying the lowering of the molecular weight will be more marked, the smaller is the content of the diene polymer in the polymer. Therefore, for polymers which do not contain diene polymers, it is desirable for the number average molecular weight to be greater than 100,000. On the other hand, there is no particular upper limit to the molecular weight, but in ordinary cases it should be 400,000 or less.

The poly(vinyl cyclohexane) resin can be obtained by ring-hydrogenating this styrene polymer in the presence of a hydrogenation catalyst with an aromatic hydrogenation function. Examples of hydrogenation catalysts which can be used in this case are metals such as nickel, cobalt, ruthenium, rhodium, platinum, palladium, etc., or their oxides, salts, complex-

es of them, and catalysts in which these are supported on activated carbon, diatomaceous earth, alumina, etc., supports. Among these, catalysts containing Raney nickel, Raney cobalt, stabilized nickel, and ruthenium, rhodium, or platinum on carbon or alumina supports are especially desirable from the point of view of their reactivities.

The ring hydrogenation reaction should be performed under a pressure of 50-250 kg/cm<sup>2</sup>, using as the solvent a saturated hydrocarbon solvent, such as cyclohexane, methyl cyclohexane, n-octane, decalin, tetralin, naphtha, etc.

Furthermore, in the ring hydrogenation of the styrene polymer, cutting of the molecular chain of the polymer occurs as a side reaction. In order to prevent this molecular chain cutting, the hydrogenation should be performed at as high a hydrogenation pressure as possible, and in a short time.

It is desirable for the ring hydrogenation rate of the aromatic ring in the ring hydrogenation reaction to be 90% or more, preferably 95% or more. If the ring hydrogenation rate is low, less than 90%, there will be problems such as a lowering of the heat resistance and an increase in the birefringence of the resin obtained, which is not desirable.

In this invention, the molecular weight of the poly(vinyl cyclohexane) resin obtained in this manner depends on the composition, molecular weight, hydrogenation conditions, etc., of the styrene polymer raw material, and its range of application differs with the composition, but ordinarily its number weight average molecular weight is greater than 50,000, and preferably greater than 60,000. From the point of view of toughness, the smaller is the content of the diene polymer, the greater is the molecular weight required. When no diene polymer is contained, the molecular weight must be greater than 60,000, preferably greater than 70,000. The upper limit of the molecular weight is prescribed by the moldability, but ordinarily it is a number average molecular weight of 300,000 or less. Moreover, its softening point is 150°C or higher, preferably 160°C or higher, measured by a thermomechanical analyzer.

The poly(vinyl cyclohexane) resin of this invention can be dehydrated by a simply drying process and molded by injection molding, etc., since it is a hydrocarbon resin. Furthermore, in molding the resin, additives such as thermal stabilizers, antioxidants, etc.,



can be added, if desired, to prevent deterioration of the resin during the molding.

In manufacturing the substrate of the optical disk of this invention, first, the additives, such as stabilizers, are added, if desired, to the aforementioned poly(vinyl cyclohexane) resin, and mixing is performed with a ribbon blender, tumbler blender, Henschel mixer, etc., after which melting and kneading are performed with a Banbury mixer, single-screw extruder, twin-screw extruder, etc., and the mixture is molded into pellets. By using the pellets obtained in this manner, one can obtain optical disk substrates with excellent transparency and heat resistance and little optical distortion.

In manufacturing the optical disk of this invention by using this kind of optical disk substrate, films of recording media, such as Te and its oxides, synthetic compounds, etc., or amorphous alloy compounds, etc., of rare earth and transition metals, such as GdFe, TbFe, GdFeCo, and TbFeCo, are formed on the surface of this substrate by metal deposition, etc., and these films can be further coated with a protective layer.

#### Actual Examples

This invention will be explained in more detail below by giving actual and comparison examples, but it is not limited by the actual examples below, as long as its gist is preserved.

In the actual and comparison examples below, the physical properties were measured by the following methods.

① Number average molecular weight:

Measured in the same manner as polystyrene, using tetrahydrofuran (THF) as the solvent, by gel permeation chromatography (GPC); the polystyrene-converted number average molecular weight was obtained.

② Ring hydrogenation rate (%):

Measured by dissolving the poly(vinyl cyclohexane) resin in tetrahydrofuran (THF) and measuring the UV absorption.

③ Softening point (°C):

Measured with a Dupont Co. thermomechanical analyzer, at a temperature rise rate of 5°C/min. The load was 5 g and the thickness of the test pieces was 3 mm.

④ Measurement of heat resistance of optical disk:

The carrier level (C/N ratio) (the case in which Al [illegible] was used was considered 0 dB) of an optical disk with a recording medium and protective layer was measured by means of a [illegible] property detector with a PIN photodiode differential detector attached. The measurement was performed before and after a heat treatment at 100°C for 2 hours, and the results were compared.

Furthermore, the recording and reproducing conditions were as follows:

Recording conditions: CAV (constant [?hard to read] angular velocity), 1800 rpm; [illegible] diameter, 30 mm position; [illegible] recording; recording frequency, 0.5 MHz; duty 50%

Reproducing conditions: CAV 1800 rpm  
reproduction power 0.8 mW

Actual Example 1

As thermal stabilizers, 0.2 part by weight tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)]propionate methane (Nippon Chiba Geigy Co., Irganox 1010) and 0.2 part by weight tetrakis (2,4-di-t-butylphenyl-4,4'-biphenylene phosphonite (same company, Irgaphos PEPQ) were added to 100 parts by weight poly(vinyl cyclohexane) with a number average molecular weight of 70,000, a ring hydrogenation rate of 99%, and a softening point of 171°C, obtained by hydrogenating a styrene homopolymer. Melting and kneading was performed at 250°C using an extruder, and pellets were made.

These pellets were formed into circular disk substrates 1.3 mm thick and 130 mm in diameter, at a resin temperature of 300°C, by using an extrusion molder ([illegible] Co. "M-140A") with a grooved stamper attached to the movable mold side.

The substrates obtained were inserted into a sputtering device. The device was first evacuated to  $8 \times 10^{-7}$  torr or less, and reactive sputtering of a Ta target was performed a mixed gas of Ar and  $O_2$ , forming an interference layer composed of  $Ta_2O_5$  (800 angstroms thick). Next, double simultaneous sputtering was performed with Ar gas, using a Tb target and an FeCo target, forming a TbFeCo recording layer (300 angstroms thick). Furthermore, a reflective layer 300 angstroms thick was formed by sputtering in Ar gas with an Al target, on which a Ti chip was placed.

The carrier level (C/N ratio) of the optical disk obtained was 60.8 dB before the heat treatment, and there was no change after the heat treatment. Furthermore, there was no change in the groove shape.

#### Actual Example 2

A poly(vinyl cyclohexane)-(ethylene-butene-1)-vinyl cyclohexane block copolymer with a number average molecular weight of 61,000, a ring hydrogenation rate of 99%, and a softening point of 165°C was obtained by ring-hydrogenating a styrene-butadiene-styrene block copolymer (butadiene content 5 wt %), produced by anionic polymerization. The substrate was molded and the recording layer was formed in the same manner as in Actual Example 1.

The carrier level (C/N ratio) before the heat treatment of the optical disk obtained was 60.5 dB, and there was no change after the heat treatment. Moreover, there was no change in the groove shape.

#### Comparison Example 1

The injection molding was performed in the same manner as in Actual Example 1 by using a poly(vinyl cyclohexane) with a number average molecular weight of 35,000, a ring hydrogenation rate of 97%, and a softening point of 156°C. As a result, the molecular weight was low and the resin was brittle, so that cracks appeared in the substrate when it was released from the mold and a normal substrate could not be obtained. Therefore, it could

not be evaluated as an optical disk.

#### Comparison Example 2

The substrate molding and recording layer formation were performed in the same manner as in Actual Example 1 by using a vinyl cyclohexane-styrene copolymer with a number average molecular weight of 80,000, a ring hydrogenation rate of 82%, and a softening point of 125°C.

When the heat treatment was performed on the optical disk obtained, the groove shape was changed, since the heat resistance was low.

The results mentioned above are shown in Table 1.